



Influence of the reaction conditions on the electrochemical promotion by potassium for the selective catalytic reduction of N₂O by C₃H₆ on platinum

Antonio de Lucas-Consuegra, Fernando Dorado ^{*}, Carmen Jiménez-Borja, José L. Valverde

Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha,
Avenida Camilo José Cela 10, 13005 Ciudad Real, Spain

Received 2 July 2007; received in revised form 19 September 2007; accepted 21 September 2007
Available online 26 September 2007

Abstract

In this work, we have investigated for the first time the selective catalytic reduction of N₂O by C₃H₆ over an electrochemical catalyst (Pt/K-βAl₂O₃). It was evaluated the influence of the reaction conditions (temperature, oxygen concentration, water vapour presence and time on stream treatment under reaction conditions) on the catalytic performance of the electrochemical catalyst. Electrochemical pumping of potassium ions to the Pt catalyst working electrode strongly increased the N₂O reduction rate, activating the catalyst at lower temperatures. However, it was found that the efficiency of the electrochemical promotion decreased as the oxygen concentration increased because of a strong inhibition of propene adsorption and a relative increase of the oxygen coverage. On the contrary, the presence of potassium ions on the Pt catalyst strongly decreased the inhibiting effect of water vapour, increasing the catalytic activity of the catalyst. In addition, the catalyst stability was confirmed by a deactivation study. It was found that a long term treatment at high temperature under operating conditions had a positive effect on the efficiency of the Pt/K-βAl₂O₃ electrochemical catalyst.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Electrochemical promotion; NEMCA effect; Selective catalytic reduction; N₂O; Pt catalyst

1. Introduction

The possibility of employing solid electrolytes to monitor surface activities of adsorbed species was first suggested by Wagner [1]. Subsequently, it has been shown that this electrochemical approach to catalysis can be employed not only to monitor, but also to control the chemical activities of surface species. This process, called non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) or electrochemical promotion of catalysis (EPOC) was discovered [2] and developed by Vayenas et al. [3,4]. It is based on the control, by an applied potential, of the catalyst work function, due to electrochemical pumping of ions (promoters) from a solid electrolyte [5,6]. This phenomenon enables to improve in a very pronounced and controlled manner the catalytic performance of a metal catalyst which allows reducing the

energy requirements (working at lower temperature) or the amount of metal (using thin films). Electrochemical promotion has been reported for over seventy catalytic reactions on a large number of catalyst electrodes interfaced to a variety of solid electrolytes and mixed electronic–ionic conductors [4]. Most of these studies deal with environmental catalysis, particularly in automotive pollution control, since it is an urgent need, especially due to likely more stringent future legislations. For instance, recent studies have explored the utility of electrochemical promotion to improve the catalytic combustion of hydrocarbons [7–12] the oxidation of CO [13,14] and the selective catalytic reduction (SCR) of NO by hydrocarbons [15–19]. Nevertheless, apart from a previous work of Marwood and Vayenas [20], there have been no further studies on electrochemical promotion for the reduction of nitrous oxide (N₂O).

Nitrous oxide has been recognised as a powerful greenhouse gas with 310 and 15 times the global warming potential of CO₂ and CH₄, respectively, and it was included in the six-gas basket defined by the United Nations Framework Convention on

* Corresponding author. Tel.: +34 926295300; fax: +34 926295318.

E-mail address: Fernando.Dorado@uclm.es (F. Dorado).

Climate Change in Kyoto (1997) [21]. In addition, the harmful effect of N₂O in our environment is further aggravated by its indirect contribution to the ozone layer depletion as the main precursor of stratospheric NO_x [22]. Hence, it is quite important to convert N₂O into harmless products. Many catalysts such as supported or unsupported noble metals, pure oxides, mixed oxides, spinels, perovskites, hydrotalcites and zeolites have been tested for direct decomposition of N₂O [23]. The main problem observed for most catalytic systems, was the inhibition of N₂O decomposition by the strong adsorption of the oxygen species produced. Selective catalytic reduction (SCR) of N₂O with light hydrocarbons (HC-SCR) has been proposed as a promising abatement alternative [24]. Addition of hydrocarbons as reducing agents facilitates the removal of atomic oxygen (deposited by N₂O), lowering the operation temperature. However, previous studies have shown [25] that the presence of O₂ and H₂O in N₂O containing tail-gases causes adverse effects on the catalyst due to inhibition or poisoning effects, thus limiting its practical application.

The aim of this work was to verify if electrochemical promotion could be a solution to reduce the adverse effects of poisons, increasing the activity of the catalyst for the removal of N₂O. Thus, we have investigated for the first time, the selective catalytic reduction of N₂O by propene over an electrochemical catalyst. The selection of Pt as the catalyst and K-βAl₂O₃ as solid electrolyte was based on previous studies which have shown the extraordinary behaviour of this electrochemical catalyst for the removal of C₃H₆ [8] and CO [13] which usually come along with N₂O in automotive exhaust emissions. Moreover, in this study, the influence of the reaction temperature, the presence of poisons such as O₂ and water steam and the influence of long term operating conditions were evaluated on the efficiency of the electrochemical catalyst.

2. Experimental

2.1. Preparation and characterization of the electrochemical catalyst

The electrochemical catalyst consisted of a porous, continuous thin Pt film (geometric area of 2.01 cm²) deposited on a side of a 20 mm in diameter and 1 mm in thickness K-βAl₂O₃ disk (Ionotec). Gold counter and reference electrodes were deposited on the other side. First, the Au counter and reference electrodes were deposited by application of thin coatings of gold paste (Gwent Electronic Materials C1991025D2), followed by calcination at 800 °C for 2 h. Then, the Pt film was deposited, as described in detail elsewhere [26], by successive steps of deposition and thermal decomposition (450 °C for 1 h) of a H₂PtCl₆ precursor solution, with a metal concentration of 0.1 M. The final Pt loading was 0.68 mg Pt/cm². The surface mole (mol of active sites) of the catalyst electrode film was determined by the electrochemical technique developed by Ladas et al. [27]. The measured Pt surface mole was found to be 4.14 × 10⁻⁷ mol Pt (163 cm²), which led to a metal dispersion of 6%.

2.2. Catalytic activity measurements

Catalytic testing was performed at atmospheric pressure in a specific quartz reactor described in a previous study [26]. The electrochemical cell was placed on a fritted quartz with 21 mm of diameter, with the counter and reference electrode facing the fritted glass. An inner quartz tube was pressed onto the Pt working electrode to insure the electrical contacts. The temperature of the catalyst was measured with a K-type thermocouple (Thermocoax) placed inside the inner quartz tube. The entire reactor was placed in a furnace (JH HEE.CC4) equipped with a heat control system (Conatec 4801). Constant voltages or currents across the cell were measured and imposed using a potentiostat–galvanostat Voltalab 21 (Radiometer Analytical). The reaction gases were Praxair certified standards of 4% C₃H₆/He, 4% N₂O/He, O₂ (99.99% purity) and He (99.999% purity), which was used as the vector gas. The gas flow was controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S) while water was introduced to the reacting stream by means of a saturator at 24 °C. The tubing down stream from the saturator was heated to 100 °C to prevent condensation. The reactants were introduced into the reactor with the following concentrations: N₂O (1000 ppm), C₃H₆ (2000 ppm), O₂ (0–1%), H₂O (0–3%) balanced with He. The overall gas flow rate was kept constant at 12 L h⁻¹. Reactant and product gases were analyzed with a microgas chromatograph (Varian CP-4900) and a chemiluminescence analyzer (Teledyne 9110 EH). Nitrogen was the only N-containing product since NO and NO₂ were not detected in this study at all. Before these analyses, the water was trapped by a condenser at -5 °C. Blank experiments showed that the catalytic rate of N₂O reduction on the solid electrolyte and on the Au auxiliary electrodes was always negligible under the operating conditions. Thus, all the potential-induced changes in the catalytic activity can be exclusively attributed to Pt.

Prior to the catalytic activity measurements, the catalyst was reduced in a stream of H₂ at 450 °C for 1 h. After the reduction process, the sample was cooled down to 200 °C under He flow. The reactive mixture flow (with 1% O₂ and 0% of H₂O) was switched into the reactor and the sample was heated to 600 °C at 5 °C min⁻¹. The catalyst was maintained at 600 °C for 12 h in order to stabilise its activity and then, the temperature was decreased to 200 °C at 5 °C min⁻¹.

3. Results

3.1. Galvanostatic and potentiostatic transient experiments

The electrochemical promotion concept of catalysis provides a simple method for the direct correspondence of the promoter coverage on catalyst surface to the value of the catalyst potential (V_{WR}). The transient galvanostatic mode of operation also provides a rapid method to link the response of the reaction rate to the promoter coverage. Fig. 1 depicts the response of the N₂O and C₃H₆ conversion along with the corresponding changes in catalyst potential under a galvanostatic transient. The experiment was carried out at 450 °C with a

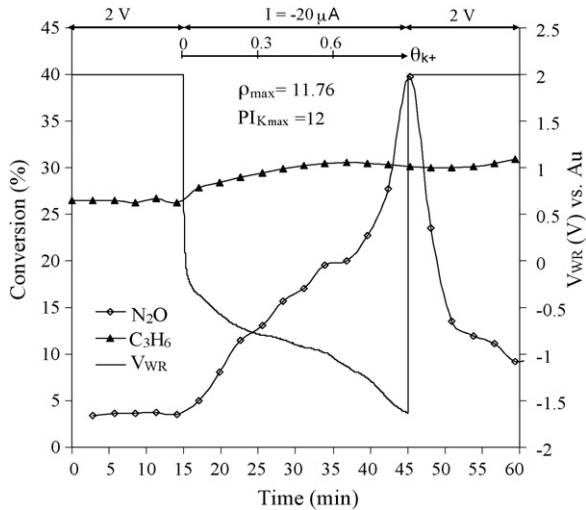


Fig. 1. Transient effect of constant applied current ($I = -20 \mu\text{A}$) on N_2O and C_3H_6 conversion and on catalyst potential (V_{WR}). Conditions: $T = 450^\circ\text{C}$, $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2$: 2000 ppm/1000 ppm/2000 ppm, He balance, total flow rate = 12 L h⁻¹.

fixed feed gas composition of $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2$: 2000/1000/2000 ppm. First, the Pt surface was electrochemically cleaned of potassium ions by application of a positive potential of 2 V until the current between the catalyst and counter electrode vanished (15 min). Then, at $t = 15$ min a negative current $I = -20 \mu\text{A}$ was applied for 30 min. Potassium ions were electrochemically transferred from the electrolyte to the Pt catalyst at a rate equal to $I/F = 2.07 \times 10^{-10} \text{ mol K s}^{-1}$. The inserted abscissa indicates the induced change in potassium coverage (θ_k) on the Pt surface, calculated using Faraday's law:

$$\frac{d\theta_k}{dt} = -\frac{I}{FN} \quad (1)$$

where F is the Faraday's constant, N is the number of Pt active sites ($4.14 \times 10^{-7} \text{ mol}$) and t is the time of current application. The maximum polarization effect on the catalytic N_2O reaction rate was characterized by the rate enhancement ratio (ρ) and the promotion index (PI_K), defined by Eqs. (2) and (3), respectively:

$$\rho = \frac{r}{r_0} \quad (2)$$

$$\text{PI}_K = \frac{\Delta r/r_0}{\Delta \theta_K} \quad (3)$$

where r_0 is the catalytic reaction rate under unpromoted conditions ($V_{\text{WR}} = 2 \text{ V}$) and r is the catalytic reaction rate under promoted ones ($V_{\text{WR}} < 2 \text{ V}$). Under these conditions (K pumping to the catalyst surface), a pronounced decrease in the catalyst potential, and consequently in the catalyst work function occurred ($e \Delta V_{\text{WR}} = \Delta \phi$) [5,28]. This was accompanied by a very marked increase ($\rho = 11.76$) in the N_2O reduction rate due to a strong electronic effect of potassium on the catalyst ($\text{PI}_K = 12$) [4]. The propene conversion was also increased with the presence of potassium promoter, exhibiting a maximum for $\theta_k \approx 0.7$. A further increase in the promoter coverage poisoned the transformation of C_3H_6 into CO_2 . It is apparent that K acted

as strong promoter for the reduction of N_2O whereas the effect on the propene oxidation rate seemed to be less important, even reaching a poisoning effect for high alkali coverages. Setting $V_{\text{WR}} = 2 \text{ V}$ at $t = 45$ min and therefore, electrochemical pumping of potassium ions to the electrolyte, gradually decreased the N_2O reduction rate while the C_3H_6 oxidation one experienced a slight increase. For both reaction rates the polarization of $V_{\text{WR}} = 2 \text{ V}$ for 15 min was not enough to achieve the initial unpromoted conversion values and therefore to return all the K^+ promoters back to the electrolyte. Such decrease of the promoter coverage induced by this latter polarization could approach to an optimum behaviour of the Pt catalyst for C_3H_6 oxidation, since as already observed, high potassium coverage poisoned it.

The described galvanostatic transient is fully consistent with the potentiostatic one shown in Fig. 2, which depicts the response of the N_2O and C_3H_6 conversion versus time to step changes in applied catalyst potential. The experiment was carried out at the same reaction conditions ($T = 450^\circ\text{C}$ and a gas composition of $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2$: 2000/1000/2000 ppm). Consecutive steps of positive ($V_{\text{WR}} = 2 \text{ V}$) and negative polarizations ($V_{\text{WR}} = -0.5 \text{ V}$ and -1 V) were applied for 2 and 4 h, respectively, in order to study the steady-state behaviour of the catalyst during long term polarization stages. The depicted positive/negative currents measured between the working electrode (catalyst) and Au counter electrode should correspond to the following anodic/cathodic reaction at the catalyst (working) electrode:



Thus, the variation of the current versus time during the potentiostatic steps displays the rate of formation and decomposition of the promoter phases during the different polarization steps. Under negative polarization, the promoter ions were electrochemically transferred from the solid electrolyte to the catalyst, leading to a cathodic electron charge transfer reaction between the ions and the different

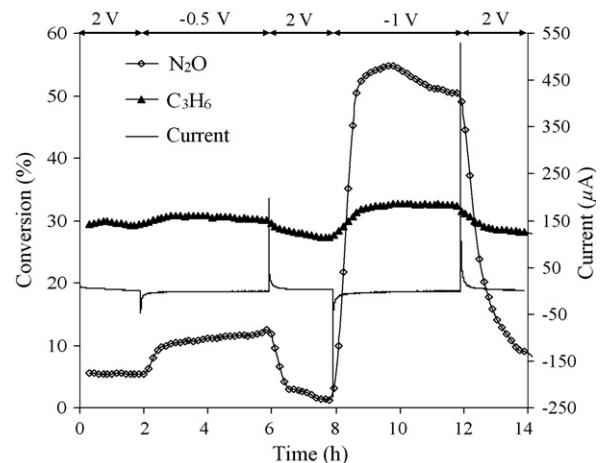


Fig. 2. Transient effect of step changes in applied potential on N_2O and C_3H_6 conversion and on the corresponding current. Conditions: $T = 450^\circ\text{C}$, $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2$: 2000 ppm/1000 ppm/2000 ppm, He balance, total flow rate = 12 L h⁻¹.

species adsorbed on the catalyst surface (negative current). However, under positive polarization, the promoter ions returned to the solid electrolyte, leading to the anodic charge transfer reaction (positive current). Therefore, the change in the direction of the electron charge transfer reaction (reaction (4)) explains the observed shifts for the current values between the different polarizations. Concerning the variation of the catalytic activity, it can be observed that starting from an electrochemically clean potassium surface ($V_{WR} = 2$ V) the application of negative polarizations always increased both the N_2O and C_3H_6 reaction rates. For instance, the application of $V_{WR} = -1$ V increased the N_2O conversion from 1.3 to 50% ($\rho = 38.46$) while the C_3H_6 conversion increased from 27 to 33% ($\rho = 1.22$). As already observed in Fig. 1, the promoting effect of potassium ions was more pronounced on the N_2O reduction rate than on the C_3H_6 oxidation one. It also is interesting to note that although the most important effect of the applied potential was attained in the first moments after the polarization, the behaviour of the electrochemical catalyst was not stable during the long term potentiostatic steps. For instance, the N_2O conversion continued increasing and decreasing after applying during 3 h, $V_{WR} = -0.5$ V and $V_{WR} = -1$ V, respectively. Such different behaviour under application of $V_{WR} = -0.5$ V and $V_{WR} = -1$ V established that the origin of such no stable behaviour of the catalytic reaction rate under polarization cannot be attributed to thermal modification of the Pt catalyst surface. The current versus time curves shown in Fig. 2 at constant applied potential, evidenced that although most of the potassium ions migrated to the catalyst in the first moments after the polarization (causing the most pronounced effect) the dynamic tendency of the current to zero was very slow (leading to a long term dynamic response on the catalytic rate).

3.2. Influence of the reaction temperature

The SCR of N_2O by C_3H_6 was investigated through a temperature-programmed reaction experiments (light-off measurements) under application of four different catalyst potentials (Fig. 3). The experiments were carried out at a fixed gas composition of $C_3H_6/N_2O/O_2$: 2000/1000/2000 ppm between 200 and 600 °C with a constant heating rate of 2 °C min⁻¹. From Fig. 3, it is clear that both N_2O (Fig. 3a) and propene conversions (Fig. 3b) were strongly temperature dependent. In addition, it can be observed, that as the catalyst potential decreased, the system could be strongly promoted above 340 °C. While for the unpromoted catalyst ($V_{WR} = 2$ V) the N_2O conversion did not exceed 17% at high temperatures (580 °C), the electrochemically promoted ones ($V_{WR} < 2$ V) exhibited higher conversions at much lower temperatures. For instance, for an applied catalyst potential of $V_{WR} = -2$ V, the temperature corresponding to 15% of N_2O conversion (T_{15}) decreased by 167 °C in comparison with the unpromoted catalyst ($V_{WR} = 2$ V). These results clearly demonstrate that electrochemical pumping of potassium ions is a suitable technique for activating the Pt catalyst at lower temperatures. A similar electrochemical activation at lower temperatures has

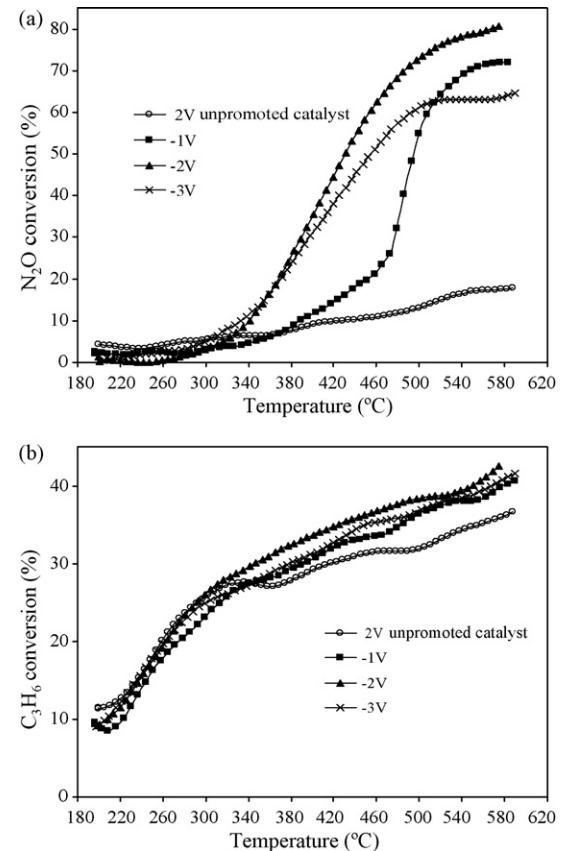


Fig. 3. N_2O (a) and C_3H_6 (b) conversion vs. reaction temperature at different catalyst potential. Conditions: $C_3H_6/N_2O/O_2$: 2000 ppm/1000 ppm/2000 ppm, He balance, total flow rate = 12 L h⁻¹.

recently been published for CO oxidation [13] over the same electrochemical catalyst ($Pt/K-\beta Al_2O_3$) which shows potential for the practical use of this electrochemical cell to remove exhaust gases at low temperature (e.g. during cold start engine regime). On the other hand, it can be observed that the application of high negative potential poisoned the catalyst above a specific reaction temperature. Thus, the application of $V_{WR} = -3$ V led to a lower N_2O reduction rate above 380 and 500 °C in comparison with $V_{WR} = -2$ V and $V_{WR} = -1$ V, respectively. In addition, the application of $V_{WR} = -3$ V led to a lower C_3H_6 oxidation rate in comparison with $V_{WR} = -2$ V above 320 °C. Nevertheless, it should be mentioned that under all explored reaction conditions the catalytic performance of the electropromoted catalyst ($V_{WR} < 2$ V) was always higher than the unpromoted one ($V_{WR} = 2$ V).

Fig. 4 shows the steady-state (potentiostatic) N_2O conversion as a function of the catalyst potential (V_{WR}) at a fixed composition of $C_3H_6/N_2O/O_2$: 2000/1000/2000 ppm for three different reaction temperatures (350, 400 and 500 °C). Initially, before the application of each potential, a positive potential of $V_{WR} = 2$ V was applied for 30 min until the current between the catalyst and the counter electrode vanished, in order to clean the catalyst surface from potassium and to define a reproducible state of the Pt catalyst surface. As expected, a decrease in the catalyst potential, strongly increased the N_2O reduction rate at intermediate reaction temperatures ($T = 400$ °C) while the

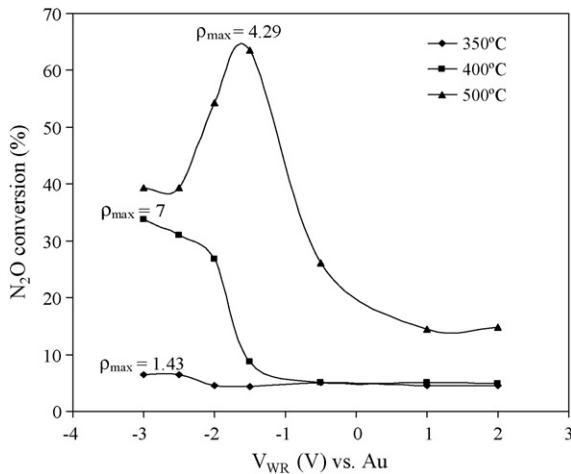


Fig. 4. Steady-state effect of the applied potential on the N_2O conversion at different reaction temperatures. Conditions: $C_3H_6/N_2O/O_2$: 2000 ppm/1000 ppm/2000 ppm, He balance, total flow rate = 12 L h⁻¹.

effect was less pronounced at lower ones ($T = 350$ °C). Thus, for both temperatures the system exhibited purely electrophilic NEMCA behaviour [4], i.e., the reaction rate increased upon negative polarization. However, at high temperatures ($T = 500$ °C) the system showed a volcano type NEMCA behaviour [4]. Under these conditions, the reaction rate showed a maximum at $V_{WR} = -1.5$ V. For this potential, the N_2O conversion strongly increased from 14.8% for the unpromoted catalyst ($V_{WR} = 2$ V) up to 63.5% for the optimally promoted one. However, a further decrease in the applied catalyst potential led to a decrease in the N_2O conversion achieving 39.5% under application of $V_{WR} = -3$ V, but still keeping a higher value of conversion than the unpromoted catalyst. Such evolution of the potentiostatic behaviour of the electrochemical catalyst with the reaction temperature is similar to that recently published [15] for the HC-SCR of NO by C_3H_6 and is fully consistent with the temperature programmed reaction results shown in Fig. 3.

3.3. Influence of the oxygen concentration

Fig. 5 shows the influence of the catalyst potential at $T = 400$ °C on the N_2O (Fig. 5a) and C_3H_6 conversion (Fig. 5b) as a function of the oxygen concentration (the other reactant concentrations were kept constant C_3H_6/N_2O : 2000/1000 ppm). It was observed that when there was no potassium promoter on the catalyst surface ($V_{WR} = 2$ V) the N_2O conversion curve exhibited a positive order dependence to the oxygen concentration for the overall studied range. However, the picture was strongly altered on K-modified Pt surfaces ($V_{WR} < 2$ V), where upon increasing the $[O_2]$ above 5000 ppm the reaction rate showed a negative order dependence for O_2 . Fig. 5a also shows that for high O_2 concentrations ($[O_2] = 1\%$) the application of negative potential and thus the presence of potassium promoter led to a poisoning behaviour of the catalyst. Nevertheless, it is interesting to note, that below 1% of O_2 , the presence of potassium on the catalyst always enhanced the N_2O reduction achieving values of the rate

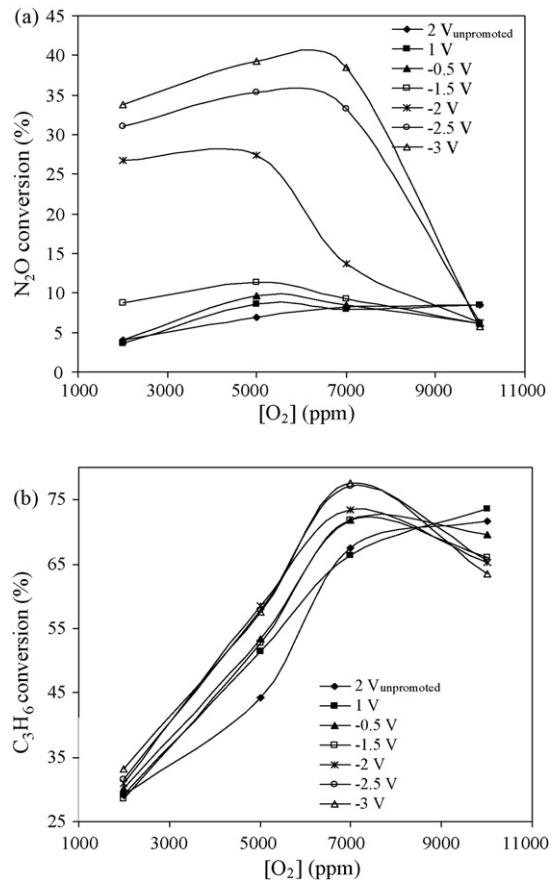


Fig. 5. Oxygen concentration effect on N_2O (a) and C_3H_6 (b) conversion at different fixed catalyst potentials. Conditions: $T = 400$ °C, C_3H_6/N_2O : 2000 ppm/1000 ppm, He balance, total flow rate = 12 L h⁻¹.

enhancement ratio close to 8. A similar trend could be observed for the effect of the O_2 concentration on the C_3H_6 conversion (Fig. 5b). While for the unpromoted conditions (positive potential) the O_2 concentration was always positive order for the C_3H_6 reaction rate in the overall studied range, it became to negative order above 7000 ppm under electropromoted conditions (negative potential). Thus, a similar influence of the O_2 concentration was found for both N_2O reduction and C_3H_6 oxidation.

Fig. 6 depicts the influence of the applied catalyst potential on the steady-state N_2O rate enhancement ratio at different oxygen concentrations. As expected, a change in the potentiostatic behaviour of the electrochemical catalyst was observed above a specific O_2 concentration. Thus, at oxygen concentrations below 1%, an electrophilic NEMCA behaviour took place, while for 1% of O_2 an electrophobic one was observed (the reaction rate decreased upon negative polarization). Along with such change on the potentiostatic behaviour of the electrochemical catalyst, an attenuation of the promoting effect can be clearly observed as the oxygen concentration increased. A similar behaviour of the promoting effect with the increase of the oxygen concentration has already been observed in previous studies of SCR of NO by C_3H_6 using $Na-\beta Al_2O_3$ [26,29] and YSZ [30] as solid electrolytes.

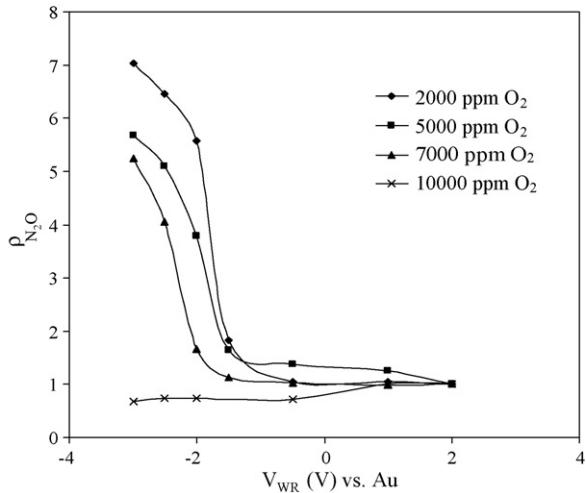


Fig. 6. Influence of oxygen concentration on the steady-state potentiostatic variation of N_2O rate enhancement ratio. Conditions: $T = 400^\circ\text{C}$, $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2$: 2000 ppm/1000 ppm/1%, He balance, total flow rate = 12 L h^{-1} .

3.4. Influence of the presence of water in the feed

Fig. 7 shows the influence of the presence of water (3%) on the potentiostatic variation of the N_2O and C_3H_6 steady-state

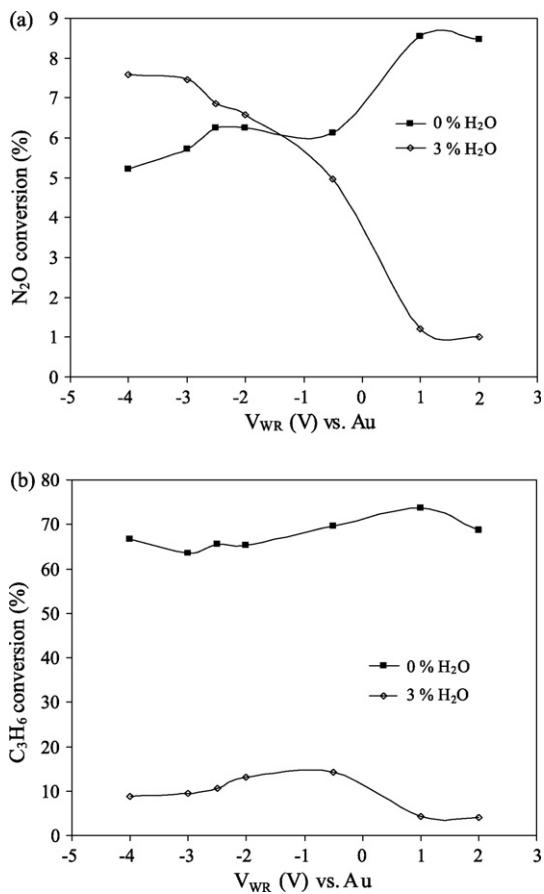


Fig. 7. Influence of the presence of water (3% H_2O) on the steady-state potentiostatic variation of N_2O (a) and C_3H_6 (b) conversion. Conditions: $T = 400^\circ\text{C}$, $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2$: 2000 ppm/1000 ppm/1%, He balance, total flow rate = 12 L h^{-1} .

conversion obtained at 400°C under fixed composition of $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2$: 2000 ppm/1000 ppm/1%. It was observed that the unpromoted catalytic activity ($V_{\text{WR}} = 2 \text{ V}$) was strongly suppressed by the presence of water in the feed. Thus, the unpromoted N_2O and C_3H_6 conversions decreased from 8.5 to 1% and from 70 to 4%, respectively, under presence of water. This behaviour, already observed for Pt based catalyst for the SCR of NO by hydrocarbons [31], suggests that the water vapour would act on the Pt active sites inhibiting the reactants adsorption. On the other hand, it was observed that the presence of water strongly modified the potentiostatic behaviour of the electrochemical catalyst. As already observed in Fig. 5, under 1% of oxygen and dry conditions, electrochemical pumping of potassium ions to the Pt catalyst upon negative polarization decreased both, N_2O and C_3H_6 reaction rates, leading to an electrophobic NEMCA effect. However, under the presence of water on the feed, electrochemical pumping of potassium ions increased both N_2O and C_3H_6 conversion, leading to electrophilic and volcano type NEMCA behaviour, respectively. Thus, under 3% of water in the feed the presence of potassium promoter enhanced the N_2O conversion from 1 to 7.5% while the C_3H_6 conversion increased from 4 to 14.5% at the optimum applied potential ($V_{\text{WR}} = -0.5 \text{ V}$). It should be pointed out that this is the first time that the NEMCA effect has been investigated for the SCR process under the presence of water in the feed and seems to be an appropriate solution to reduce the adverse effects of poisons, increasing the activity of the catalyst. Thus, while under unpromoted reaction conditions, i.e., under positive potential, water vapour acted as a strong poison on the catalyst, under negative potential, the poisoning effect is not longer observed.

In order to characterize the nature of the different adsorbates that participate in the reaction, the variation of the open circuit potential (V_{WR}^o) versus time at 400°C was measured under a changing gas atmosphere (Fig. 8). The measure voltage represented the open circuit potential difference between the catalyst potential and that of the gold reference electrode, both exposed to the gas atmosphere. It was observed that the

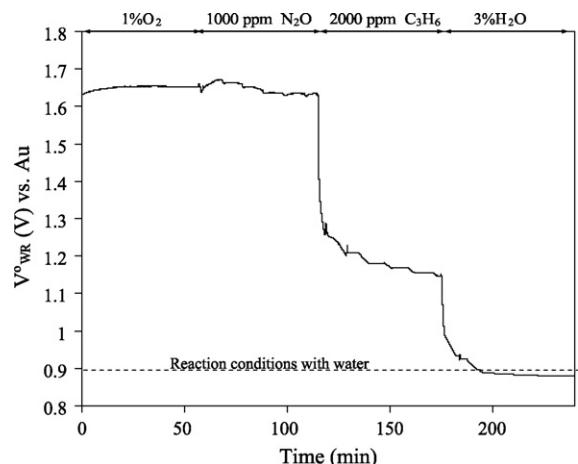


Fig. 8. Influence of the reaction atmosphere on the open circuit potential (V_{WR}^o) at 400°C . Reaction conditions with water denotes: $T = 400^\circ\text{C}$, $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2/\text{H}_2\text{O}$: 2000 ppm/1000 ppm/1%/3%, He balance, total flow rate = 12 L h^{-1} .

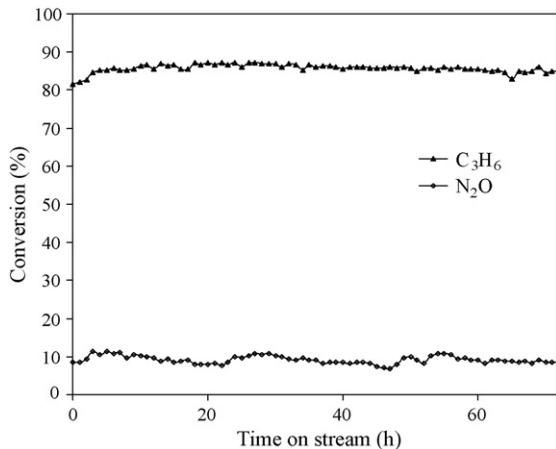


Fig. 9. Influence of time on stream on N_2O and C_3H_6 conversion during the long term thermal treatment. Conditions: $T = 650^\circ\text{C}$, $\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2/\text{H}_2\text{O}: 2000 \text{ ppm}/1000 \text{ ppm}/1\%/3\%$, He balance, total flow rate = 12 L h^{-1} .

presence of different adsorbed species on the catalyst surface strongly modified the open circuit potential (V_{WR}°). Depending on the change that chemisorbed species induces on the open circuit potential and consequently on the catalyst work function ($e\Delta V_{\text{WR}} = \Delta\phi$) of the Pt catalyst surface, a major distinction can be made between electropositive (electron donor) and electronegative (electron acceptor) adsorbates [4]. It can be clearly observed that while O_2 and N_2O maintained a high positive open circuit potential (electronegative adsorbates), C_3H_6 and H_2O strongly decreased it (electropositive adsorbates). In addition, it was observed that the value of the open circuit potential under the presence of all the reactants (reaction conditions) was almost the same as the value of the open circuit potential under the exclusive presence of water. This fact demonstrated, as previously mentioned, that under the

explored reaction conditions, water was strongly adsorbed on the Pt catalyst active sites inhibiting the adsorption of the other reactants.

3.5. Deactivation study of the electrochemical catalyst

The aim of this study was to evaluate the catalyst durability against thermal sintering which is necessary for any catalyst formulation, as well as the influence of the long term treatment under operating conditions on the efficiency of the electrochemical catalyst. In this point, the catalytic activity of the electrochemical catalyst was tested after a long term stability treatment under reaction conditions ($\text{C}_3\text{H}_6/\text{N}_2\text{O}/\text{O}_2/\text{H}_2\text{O}: 2000 \text{ ppm}/1000 \text{ ppm}/1\%/3\%$) carried out at high temperature (650°C) for 3 days. Fig. 9 shows the variation of N_2O and C_3H_6 conversion during the long term thermal treatment. It was observed that both N_2O and C_3H_6 conversions were kept constant during the long term treatment on stream. It is demonstrated that the wet impregnation procedure led to a Pt film with good resistance to the thermal sintering even during long term treatment at high temperature under presence of water vapour.

Fig. 10 shows the transient responses for the N_2O reduction at 400°C over the $\text{Pt}/\text{K}-\beta\text{Al}_2\text{O}_3$ electrochemical catalyst under a changing reaction gas atmosphere for the unpromoted ($V_{\text{WR}} = 2 \text{ V}$) and electropromoted conditions ($V_{\text{WR}} = -2 \text{ V}$) after the long term stability experiment. Thus, the electrochemical catalyst was exposed to different reaction compositions stages for 1.5 h each one. At stage I, only N_2O was supplied. Under these conditions, the unpromoted and promoted catalyst exhibited the same activity due to the thermal catalytic decomposition of N_2O . At stage II, C_3H_6 was added to the stream. The unpromoted catalyst experienced a slight increased while the promoted one was strongly activated.

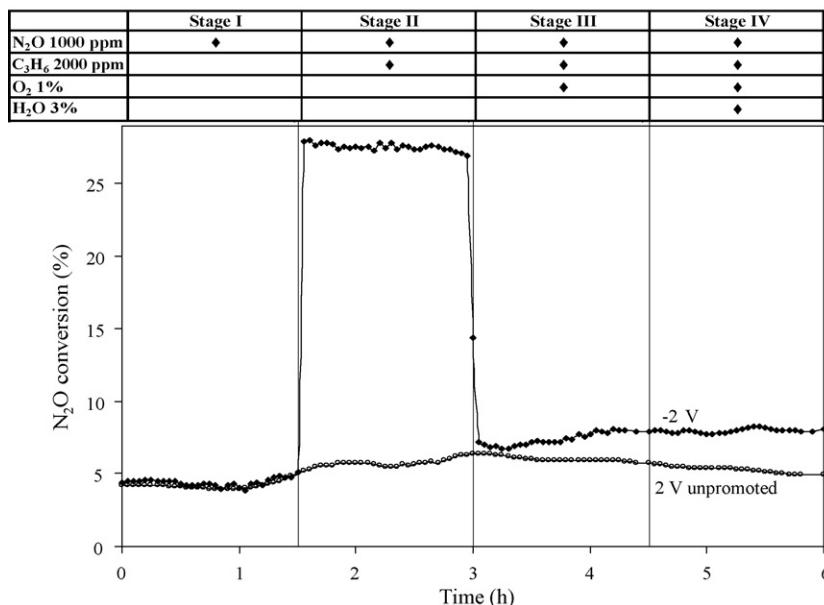


Fig. 10. Transient responses of the unpromoted ($V_{\text{WR}} = 2 \text{ V}$) and promoted ($V_{\text{WR}} = -2 \text{ V}$) $\text{Pt}/\text{K}-\beta\text{Al}_2\text{O}_3$ electrochemical catalyst to a changing reaction atmosphere after the long thermal treatment. Conditions: $T = 400^\circ\text{C}$, total flow rate = 12 L h^{-1} .

Table 1

Influence of the long term thermal treatment on the N₂O rate enhancement ratio (ρ) and on the N₂O promoted conversion at $V_{WR} = -2$ V ($X_{N_2O}^P$) under dry and wet conditions

	[H ₂ O] = 0%		[H ₂ O] = 3%	
	Before	After	Before	After
ρ	0.74	1.40	7.40	1.67
$X_{N_2O}^P$	6.25	8.00	7.50	8.23

Conditions: $T = 400$ °C, C₃H₆/N₂O/O₂/H₂O: 2000 ppm/1000 ppm/1%/0–3%, He balance, total flow rate = 12 L h⁻¹.

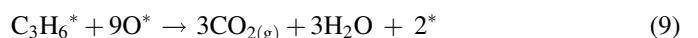
Under these conditions, the presence of electrochemical promoter on the catalyst strongly increased the catalytic activity ($\rho = 4.21$). At stage III, the addition of O₂ decreased both the unpromoted and promoted catalyst. As expected, the decrease under electropromoted conditions was higher than for the unpromoted one, in good agreement with Fig. 5. Nevertheless, at this point, the presence of electrochemical promoter still enhanced the catalytic activity ($\rho = 1.4$). Finally, at stage IV, water was also fed. As previously observed in Fig. 7, the presence of water on the stream produced an additional decrease on the catalytic activity of the unpromoted catalyst. However, under electropromoted conditions, the catalyst kept the same catalytic performance reaching a value of the rate enhancement ratio of $\rho = 1.7$. The most important point was that after the long term thermal treatment, the Pt catalyst was still activated by the negative polarization.

Table 1 compares (before and after) the influence of the long term thermal treatment on the N₂O rate enhancement ratio (ρ) and on the N₂O conversion under promoted conditions at $V_{WR} = -2$ V ($X_{N_2O}^P$) under dry and wet reaction atmospheres ($T = 400$ °C, C₃H₆/N₂O/O₂/H₂O: 2000 ppm/1000 ppm/1%/0–3%). Some differences could be observed between the catalytic performance of the electrochemical catalyst before and after the long term treatment at high temperatures. Thus, while under 1% of O₂ and dry conditions the presence of potassium promoter produced a slight decrease ($\rho = 0.74$) on the catalytic activity before the long term treatment, after it, the presence of potassium promoter increased the N₂O reduction rate ($\rho = 1.40$). On the other hand, the efficiency of electrochemical promotion to improve the catalytic activity of the catalyst under presence of water also changed after the long term thermal treatment. Thus, while before the long term thermal treatment under presence of water the presence of promoter strongly increased the N₂O reduction rate ($\rho = 7.4$), after it, the Pt catalyst was only slightly improved by the presence of potassium promoter ($\rho = 1.67$). Nevertheless, as observed in Table 1, under all explored reaction conditions, i.e., O₂/H₂O: 1/0% and O₂/H₂O: 1/3% (keeping constant the other reactant concentrations: C₃H₆/N₂O: 2000/1000 ppm) the N₂O conversion under promoted conditions ($X_{N_2O}^P$) was improved after the long thermal treatment. From these results, one can conclude that the long term treatment under reaction conditions has a positive effect on the catalytic performance of the Pt/K-βAl₂O₃ electrochemical catalyst for the SCR of N₂O by C₃H₆.

4. Discussion

This study illustrates the effect of electrochemical promotion by potassium of Pt catalyst for the reduction of N₂O by propene. The influence of the reaction conditions: temperature, oxygen concentration, water vapour presence and time on stream treatment under reaction conditions, was evaluated on the catalytic performance for the electrochemical catalyst.

In order to explain the electrochemically induced modifications on Pt catalytic activity, it is necessary to consider the reaction mechanism of the N₂O reduction over Pt. N₂O is a relatively stable molecule [23] and the main catalytic action is originated from charge donation into the antibonding orbitals, weakening the N–O bond and lowering the activation energy. Thus, the reaction of N₂O on an active catalyst is generally described as the chemisorption of N₂O via its terminal N on the substrate, leading to a scission of the N–O bond [32]. Previous works have confirmed that the formation of N₂ would arise from the breaking of the N–O bond and not from the combination of two N atoms adsorbed on the surface [33,34]. Thus, the following sequence is generally proposed to describe the selective catalytic reduction of N₂O by hydrocarbons [35]:



It is well known [15,19,26,36,37] that under propene and nitrogen oxides reactive mixtures, the Pt surface is predominantly covered by propene or by propene-derived carbonaceous species that are strongly adsorbed on the active sites (reaction (7)). Hence, as long as propene conversion keeps low (reaction (9)), the catalytic process of N₂O reduction by C₃H₆ is limited by the number of active sites covered by N₂O^{*} (reaction (5)). Our results have shown that under low oxygen concentration (Figs. 1–4) the application of negative overpotentials led to a significant enhancement of the activity of the catalyst. As discussed in previous studies [8,16,38–40], electropositive promoters (alkalis) on Pt-group metal surfaces strengthen the chemisorptive bonds of electron acceptor adsorbates (electronegatives), promoting their adsorption and weaken the chemisorptive bonds of electron donor adsorbates (electropositives). Thus, the decrease of the catalyst potential to the Pt electrode enhanced the catalytic activity of the catalyst by increasing the coverage of electron–acceptor species (O₂ and N₂O) at the expense of electron–donor (C₃H₆ and H₂O). As observed in Figs. 1–3, potassium ions acted as a strong promoter for the reduction of N₂O, whereas the effect on the propene oxidation rate seemed to be less important, even reaching a poisoning effect for high alkali coverages. This fact could be attributed to a strongly increase of the relative coverage between O and C₃H₆ ($\theta_O/\theta_{C_3H_6}$) that take place under

the presence of potassium ions. Under negative polarizations, propene adsorption decreases (reaction (9)) while the O^{*} coverage on the Pt surfaces strongly increases. This large supply of O^{*} is due to both: an increase of the O₂ adsorption (reaction (8)), and N₂O dissociation (reaction (5)) induced by the K⁺ ions promoters. These effects are responsible of the large increase of the N₂O reduction rate induced by electropositive promoters and have been discussed in detail by Lang et al. [40]. Therefore, the promotional effect of potassium on the C₃H₆ oxidation rate is attenuated due to a decrease of the number of active sites covered by C₃H₆^{*} (reaction (7)). Such behaviour differs from that previously observed under C₃H₆/O₂ atmosphere over Pt/K-βAl₂O₃ electrochemical catalyst [8] where a large increase for the propene oxidation rate was observed under electropromoted conditions. This fact can be explained taking into account the absence of N₂O in the previous work [8]. As already reported [41], the oxygen species produced from the N₂O dissociation are strongly adsorbed on the catalyst and, therefore, they could be responsible of a stronger C₃H₆ adsorption inhibition not shown in absence of N₂O under negative potentials. Such adsorption inhibition is more pronounced as the catalyst potential decrease (the strength of the Pt–O bond increases under negative polarization) and could be responsible of the poisoning effect on propene conversion observed on Figs. 1 and 3b above certain potassium coverage. A similar poisoning effect can be observed for the N₂O reduction at very negative potentials above certain reaction temperatures (Fig. 3). This fact, responsible of the change in the potentiostatic behaviour of the electrochemical catalyst at high temperatures (Fig. 4) was due to a relative increase of the surface coverage of oxygen adsorbed atoms at the expense of C₃H₆ and N₂O molecules [15]. Under propene, nitrogen oxides and oxygen reaction atmosphere, the oxygen coverage on the catalyst increases with the reaction temperature and, therefore, with the propene conversion [15,42]. In addition, it is well known [29] that electropositive adsorbates enhance the oxygen adsorption more strongly than nitrogen oxides. As a consequence, increasing the reaction temperature under promoted conditions resulted in a relative increase of the surface coverage of oxygen adsorbed atoms at the expense of C₃H₆ and N₂O molecules, thus causing a decrease in the level of promotion. This explanation can be extended to explain the observed decrease of the promotional effect as the oxygen concentration in the feed increases. These results, already observed in previous studies on SCR of nitrogen oxides by hydrocarbons [26,29,30], can be confirmed by the decrease of the propene consumption rate over K-modified Pt surface above 7000 ppm of O₂ (Fig. 5), concentration above which the potentiostatic behaviour of the electrochemical catalyst changed (Fig. 6). On the other hand, it has been observed that the presence of water strongly modifies the potentiostatic behaviour of the electrochemical catalyst. The presence of water in the feed strongly decreased the Pt catalytic activity under unpromoted conditions. This fact can be easily explained taking into account that water is strongly adsorbed on the catalytic active sites [31]. Therefore, the markedly increase for the N₂O reduction rate upon negative polarization is due to a

decrease of the H₂O coverage (electron donor specie), thus increasing the coverage of N₂O and O₂.

The resistance against water is an important factor to develop any catalyst with potential for nitrogen oxides removal. The long term thermal treatment for 3 days has clearly shown that the catalyst has a significant resistance to thermal sintering at high temperature (650 °C) even under presence of water. In addition, a slight increase of the electrochemical catalyst performance was observed after the long term thermal treatment (Table 1). It could be attributed to a slight sintering of the Pt particles under those reaction conditions. In fact, the particle size measured by XRD before and after the long term thermal treatment was of 35 and 42 nm, respectively. It is well established [43] that the strength of Pt–O bonds significantly decreases when the Pt particles size increases. Therefore, one can suggest that oxygen atoms were more strongly adsorbed on the Pt film before the long term thermal treatment than after it. It could explain the opposite behaviour of electrochemical pumping of potassium ions to the Pt catalyst before and after the thermal treatment under C₃H₆/N₂O/O₂: 2000 ppm/1000 ppm/1%. In addition, we could suggest that the slight increase on the Pt particle size after the thermal treatment could lead to a lower water adsorption on the catalyst. It would explain not only the slight improvement of the efficiency of the electrochemical catalyst after the long thermal treatment but also the different value of the rate enhancement ratio at V_{WR} = −2 V obtained before and after it (Table 1). We propose that before the long term thermal treatment, the water adsorption on the catalyst was very high. It can be drawn from the strong decrease of the N₂O conversion (from 8 to 0.8%) under unpromoted and wet conditions (Fig. 7a). In this case, the presence of potassium promoters led to a strong activation of the catalyst since the water adsorption was strongly inhibited. However, after the long term thermal treatment, the effect of catalyst polarization was less pronounced, which could be attributed to a lower initial coverage of water molecules. In fact, when water was fed again under unpromoted conditions after the long term thermal treatment (Fig. 10), it led only to a slight N₂O conversion decrease (from 5.7 to 5). This assumption is in good agreement with the recent identified rules of chemical/electrochemical promotion [4,44], as the effect of addition of a promoter on the catalytic activity depends on the initial coverage on the catalyst of the different molecules that participate in the reaction. This point clearly evidences that the electropromotion efficiency is strongly structure sensitive [17]. It is also interesting to note that the phenomenon of electrochemical promotion is effective to improve the behaviour of the Pt catalyst for the SCR of N₂O, but it is ineffective to improve the behaviour for the thermal decomposition of N₂O (Fig. 10). It demonstrates that O^{*} coming from the N₂O dissociation (reaction (6)) was strongly adsorbed on the catalyst and its removal to generate free active sites where N₂O can be adsorbed was the rate determining step. Therefore, the application of negative potential did not increase the N₂O reduction rate in the absence of C₃H₆ because although the N₂O adsorption and dissociation were favoured (reactions (5) and (6)), the strength of the Pt–O bond was also increased (even in a more pronounced way [29]) inhibiting the adsorption of new N₂O molecules.

5. Conclusions

Pt/K- β Al₂O₃ electrochemical catalyst can reach a high catalytic activity for the SCR of N₂O by propene. The efficiency of electrochemical promotion to improve the catalytic performance of the system depends on the reaction conditions. At low oxygen concentration, the presence of potassium promoter strongly increased the catalytic activity, activating the catalyst at much lower temperatures. However, as the oxygen concentration increased, the promotional phenomenon decreased even achieving a regime where the alkali metal induced poisoning. On the other hand, we have found that electrochemical promotion is a promising technique to decrease the poisoning effect of water on the catalyst. The presence of potassium ions, decreased the water adsorption on the catalyst (electropositive adsorbate), leading to an activation of the catalyst. In addition, the deactivation study showed that the wet impregnation procedure led to a Pt film with good resistance to thermal sintering under wet reaction conditions.

Acknowledgements

Financial support by the Ministerio de Educación y Ciencia of Spain (Projects: CTQ2004-07350-C02-01/PQ and CTQ2007-62512/PPQ) and the European Marie-Curie EFE-POC project (MSCF-CT-2006-046201) are gratefully acknowledged.

References

- [1] C. Wagner, *Adv. Catal.* 21 (1970) 323.
- [2] M. Stoukides, C.G. Vayenas, *J. Catal.* 70 (1981) 137.
- [3] C.G. Vayenas, S. Bebelis, S. Ladas, *Nature (London)* 343 (1990) 625.
- [4] C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsipakides, *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions*, Kluwer Academic/Plenum, New York, 2001.
- [5] C.G. Vayenas, S. Bebelis, I.V. Yentekakis, H.-G. Lintz, *Catal. Today* 11 (1992) 303.
- [6] I.V. Yentekakis, G. Moggridge, C.G. Vayenas, R.M. Lambert, *J. Catal.* 146 (1994) 292.
- [7] A. Billard, P. Vernoux, *Top. Catal.* 44 (2007) 369.
- [8] A. de Lucas-Consuegra, F. Dorado, J.L. Valverde, R. Karoum, P. Vernoux, *J. Catal.* 251 (2007) 474.
- [9] D. Pouliki, G.C. Mather, I.S. Metcalfe, *Solid State Ionics* 178 (2007) 675.
- [10] S. Bebelis, N. Kotsopoulos, *Solid State Ionics* 117 (2006) 2205.
- [11] C. Koutsodentis, A. Katsaounis, J.C. Figueroa, C. Cavalca, C.J. Pereira, C.G. Vayenas, *Top. Catal.* 38 (2006) 157.
- [12] E.A. Baranova, A. Thursfield, S. Brosda, G. Fóti, Ch. Comninellis, C.G. Vayenas, *Catal. Lett.* 105 (2005) 15.
- [13] A. de Lucas-Consuegra, F. Dorado, J.L. Valverde, R. Karoum, P. Vernoux, *Catal. Commun.* 9 (2008) 17–20.
- [14] J. Poppe, S. Volkenning, A. Schaak, E. Schutz, J. Janek, R. Imbihl, *Phys. Chem.* 1 (1999) 5241.
- [15] F. Dorado, A. de Lucas-Consuegra, C. Jiménez, J.L. Valverde, *Appl. Catal. A* 321 (2007) 86.
- [16] G. Goula, P. Katzourakis, N. Vakakis, T. Papadim, M. Konsolakis, M. Tikhov, I.V. Yentekakis, *Catal. Today* 127 (2007) 199.
- [17] P. Vernoux, F. Gaillard, R. Karoum, A. Billard, *Appl. Catal. B* 73 (2007) 73.
- [18] S. Balomenou, D. Tsipakides, A. Katsaounis, S. Thiemann-Handler, B. Cramer, G. Foti, Ch. Comninellis, C.G. Vayenas, *Appl. Catal. B* 52 (2004) 181.
- [19] P. Vernoux, F. Gaillard, C. Lopez, E. Siebert, *J. Catal.* 217 (2003) 203.
- [20] M. Marwood, C.G. Vayenas, *J. Catal.* 170 (1997) 275.
- [21] Kyoto Protocol to the United Nations Framework Convention on Climate Change, Annex A, Kyoto, Japan, December 1997 (Available online at: <http://unfccc.int/resource/docs/convkp/kpeng.pdf>).
- [22] M.B. McElroy, J.C. McConnell, *J. Atoms. Sci.* 28 (1971) 1095.
- [23] F. Kapteijn, J. Rodriguez-Mirasol, J.A. Moulijn, *Appl. Catal. B* 9 (1996) 25.
- [24] J. Pérez-Ramírez, F. Kapteijn, *Appl. Catal. B* 47 (2004) 177.
- [25] M.N. Debbagh, C.S.M. de Lecea, J. Pérez-Ramírez, *Appl. Catal. B* 70 (2007) 335.
- [26] F. Dorado, A. de Lucas-Consuegra, P. Vernoux, J.L. Valverde, *Appl. Catal. B* 73 (2007) 42.
- [27] S. Ladas, S. Bebelis, C.G. Vayenas, *Surf. Sci.* 251 (1991) 1062.
- [28] F.J. Williams, A. Palermo, S. Tracey, M.S. Tikhov, R.M. Lambert, *J. Phys. Chem. B* 106 (2002) 5668.
- [29] F.J. Williams, M.S. Tikhov, A. Palermo, N. Macleod, R.M. Lambert, *J. Phys. Chem. B* 105 (2001) 2800.
- [30] B. Béguin, F. Gaillard, M. Primet, P. Vernoux, L. Bultel, M. Hénault, C. Roux, E. Siebert, *Ionics* 2 (2002) 128.
- [31] S.-C. Shen, S. Kawi, *Appl. Catal. B* 45 (2003) 63.
- [32] G. Centi, L. Dall'olio, S. Perathoner, *Appl. Catal. A* 194 (1995) 79.
- [33] W.A. Brown, R.K. Sharma, D.A. King, S. Haq, *J. Phys. Chem.* 100 (1996) 12559.
- [34] S. Haq, A. Hodgson, *Surf. Sci.* 463 (2000) 1.
- [35] J. Perez-Ramirez, E.V. Kondratenko, M.N. Debbagh, *J. Catal.* 233 (2005) 442.
- [36] R. Burch, T.C. Watling, *Catal. Lett.* 43 (1997) 19.
- [37] R. Burch, J.A. Sullivan, T.C. Watling, *Catal. Today* 42 (1998) 13.
- [38] I.V. Yentekakis, A. Palermo, N. Filkin, M.S. Tikhov, R.M. Lambert, *J. Phys. Chem. B* 101 (1997) 3759.
- [39] A. Palermo, R.M. Lambert, I.R. Harkness, I.V. Yentekakis, O.A. Marina, C.G. Vayenas, *J. Catal.* 161 (1996) 471.
- [40] N.D. Lang, S. Holloway, J.K. Norskov, *Surf. Sci.* 150 (1985) 24.
- [41] V.K. Tzitzios, V. Georgakilas, T.N. Angelidis, *J. Chem. Technol. Biot.* 80 (2005) 699.
- [42] X. Li, F. Gaillard, P. Vernoux, *Ionics* 11 (2005) 103.
- [43] S. Benard, L. Retailleau, F. Gaillard, P. Vernoux, A. Giroir-Fendler, *Appl. Catal. B* 55 (2005) 11.
- [44] S. Brosda, C.G. Vayenas, J. Wei, *Appl. Catal. B* 68 (2006) 109.